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COMPARISON OF REACTION RATE CONSTANTS FOR UREA IN UNSATURATED AND FLOODED SOIL CONDITIONS

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ABSTRACT

Urea is the main form of nitrogen fertilizer. An in-situ study was conducted to measure the movement and transformation of urea in unsaturated soils. An important step in analytical modeling is the determination of model parameters such as reaction rate constants. To estimate the reaction rate constants, Ammonia volatilized from soil spiked with urea is collected and analyzed periodically. Partial differential equations representing urea reactions were solved using risk solver platform in the MS-Excel environment. The estimated reaction rate constant for ammonia volatilization was found to give a good estimate of volatilized ammonia with that of the observed volatilized ammonia. The estimated reaction rate constants of urea hydrolysis, distribution coefficient, ammonia volatilization, and nitrification are 0.067h $^{-1}$***, 0.668 m*** ^{3}***/g, 0.013h*** $^{-1}$ ***and 0.0029h*** $^{-1}$ ***respectively. The reaction rate constants estimated in unsaturated soil conditions are compared with flooded conditions. From the results, urea hydrolysis and Ammonia volatilization are higher in the unsaturated soil condition than the flooded soil condition. Distribution coefficient and nitrification coefficient are higher in flooded soil condition than unsaturated soil condition.***

KEYWORDS: Urea, Nitrogen Transformation, Reaction Rate Constants & Unsaturated Soils

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Original Article

INTRODUCTION

Urea is the primary nitrogen fertilizer used by farmers for almost all crops. Urea will easily dissolve in water. When urea dissolves in water it converts into ammonium by hydrolysis process. Part of this ammonium gets volatilized into ammonia and lost into the atmosphere; Part of ammonium is taken up by plants. The ammonium that has not taken up by plants converts into nitrate by nitrification process. A part of nitrate is taken up by plants; remaining nitrate is leached out of the root zone and reaches the groundwater. For proper scheduling of nitrogen fertilizer, these losses need to be calculated. Conversion of urea into ammonium, ammonia, and nitrate depends on the reaction rate constants as shown in Figure 1.

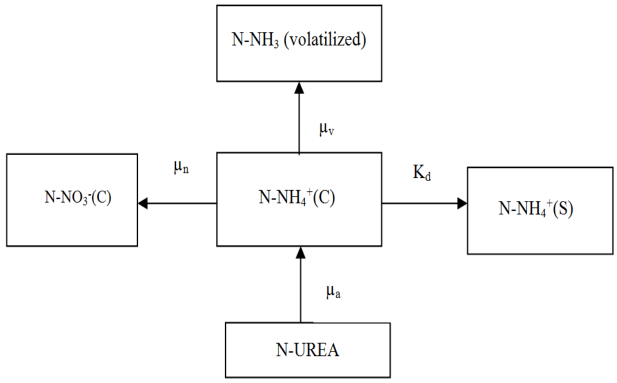

Figure 1: N Transformation Process

To find these reaction rate constants different experiments were carried out over the period of time. Factors affecting reaction rate constants are moisture content, soil type, and temperature. Bolado et al., (2005) conducted the analysis to find the reaction rate constant for sandy soil and sandy clay loam soil at 28^{o}C and 18^{o}C at the different moisture content in the laboratory conditions. Hemalatha et al., (2013) conducted the reaction rate constant experiment for different initial urea concentration for unsaturated soils under field conditions. Vanitha et al., (2017) predicted the reaction rate constant under saturated soil conditions. In the present study reaction rate constants was found for unsaturated soil conditions and compared with Hemalatha's unsaturated reaction rate constant and Vanitha's saturated reaction rate constant.

MATERIALS AND METHODS

Experimental Setup

An experiment was carried out in 500 ml of glass bottles. Bottles were arranged as shown in Figure 2. There was a diaphragm pump to force the air into bottles. B_1 is the safety trap to prevent any reflux of liquid in case of system failure. The safety trap is followed by bottle B_2 containing distilled water for humidification of the air. It is followed by bottle B_3 containing Boric acid to absorb the ammonium that may be present in the inlet air. It is followed by bottles containing soils treated with urea (B_4, B_5, B_6, & B_7). The air exiting from bottles containing soil with urea was passed through 2% boric acid solution in B_8 and B_9 bottles in order to collect the volatilized ammonium. Emission of volatilized ammonia was determined by periodic titration of the boric acid solution collected from B_8 and B_9 bottles against 0.1 N H_2SO_4. The experimental procedure was adopted from Bolado et al., (2005). The experimental setup is kept under field capacity for unsaturated conditions.

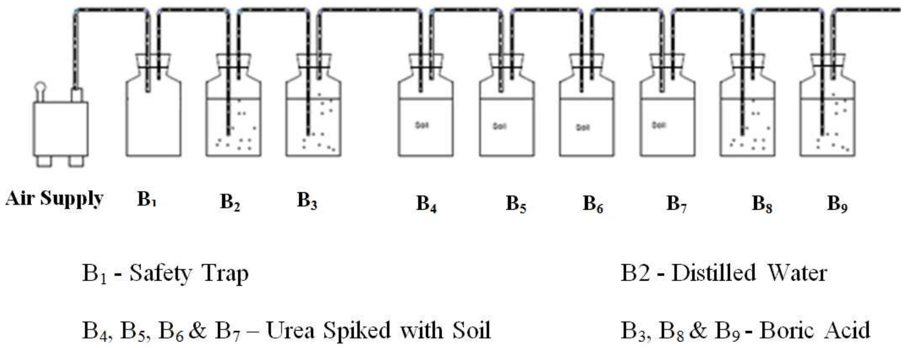

Figure 2: Experimental Setup for Estimation of Reaction Rate Constant

Table 1: Initial Conditions Employed for Finding Out the Reaction Rate Constants for Urea under Different Experiments

	Duration of Experiment	U_o (mg. N/cm^3)	Soil	Volumetric Soil Moisture Content (cm^3/cm^3)	Temperature (^{o}C)	Final Concentration of NH_4-N in Soil mg. N/cm^3	Final Concentration of NO_3-N in Soil mg. N/cm^3
Current experiment	May & June 2017	20.9	SL	0.29	38-43.5^{o}C	0.48	0.084
Vanitha et al., 2017	August & September 2016	22.15	SL	0.68	34-36^{o}C	0.80	0.109
Hemalatha et al., 2011	June 2011	37.04	SCL	0.33	25-28^{o}C	1.52	6.5

Initial experimental conditions adopted by the different researcher are given in Table 1. The results obtained from the experiment was analyzed using excel add-on package Risk solver platform. The reaction rate constants were estimated by solving the partial differential equations representing urea reactions. Partial differential equations for urea reaction can be referred from Vanitha et al.,(2017).

RESULTS AND DISCUSSIONS

The experiment was carried out from 22nd May to 21st June 2017. During the experiment, the soil temperature recorded ranges from 38°C to 43.5°C. The bulk density of soil is 1.58 (gm/cm^3) and volumetric moisture content is 0.29 (cm^3/cm^3), in which the moisture content is equal to field capacity. The soil temperature readings were recorded at 9.30 AM and 2.30 PM. Figure 3 shows the soil temperature variation during the experiment period.

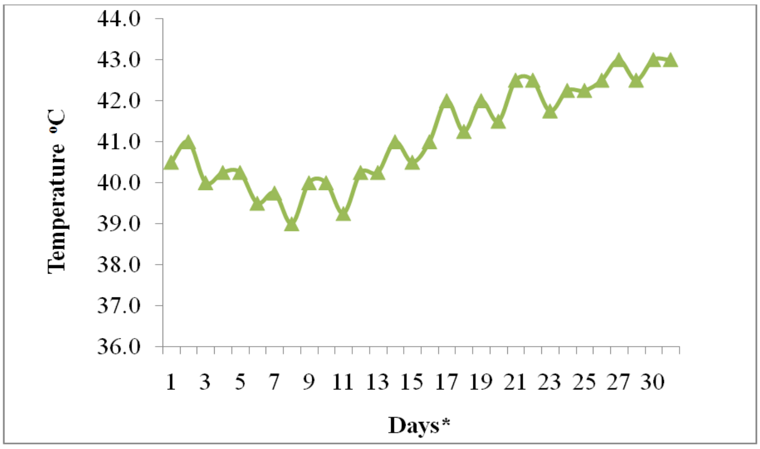

Figure 3: Temperature During the Experimental Period (*Day 1 Corresponds to May 22, 2017)

From the reaction rate experiment the estimated cumulative ammonia volatilized is 17.89 mg(N)/cm^3 in the current study as shown in Figure 4. Cumulative ammonia volatilized under flooded condition reported by Vanitha et al.,(2017) was 8 mg(N)/cm^3 as shown in Figure 5. Cumulative ammonia volatilized under unsaturated condition reported by Hemalatha is 6.05 mg (N)/cm^3 as shown in Figure 6.

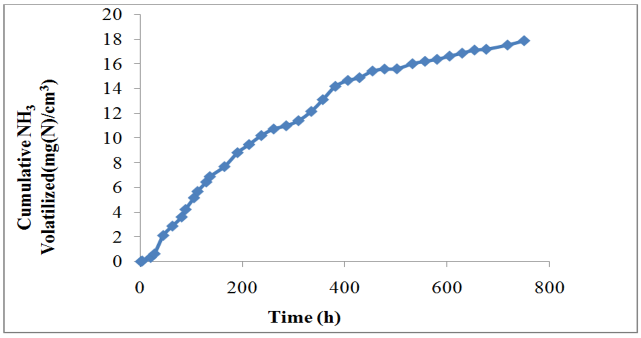

Figure 4: Cumulative Ammonia Volatilized in Unsaturated Condition (Current Experiment)

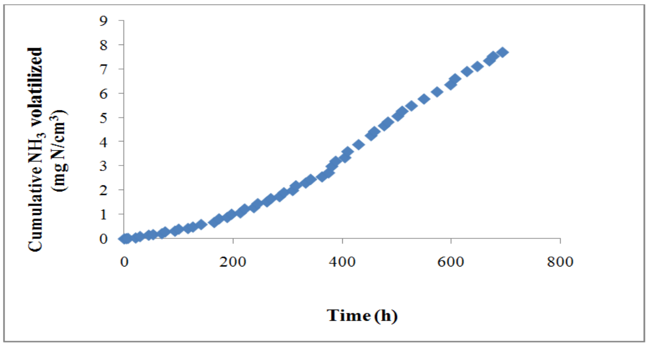

Figure 5: Cumulative Ammonia Volatilized Under Flooded Condition (Vanitha et al., 2017)

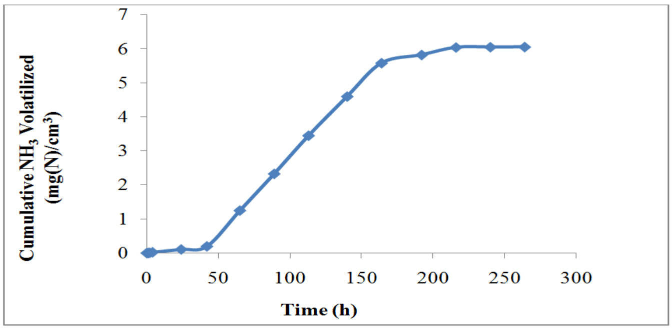

Figure 6: Cumulative Ammonia Volatilized under Unsaturated Condition (Hemalatha et al., 2013)

Table 2: Comparison of Reaction Rate Constants for Urea Transformation

N Transformation Processes	Urea Hydrolysis (μ_a)(h^{-1})	Distribution Coefficient (K_d) (cm^3/g of Soil)	Ammonia Volatilization (μ_v) (h^{-1})	Nitrification (μ_n) (h^{-1})
Estimated Values Unsaturated Condition (Current experiment)	0.067	0.668	0.013	0.0029
Unsaturated Condition (Hemalatha et al.,)	0.139	0.03386	0.0083	0.0074
Flooded condition (Vanitha et al.,)	0.0022	0.9	0.0081	0.01

Results obtained from experiments are compared with the available literature values (Table 2). Urea hydrolysis rate constant (μ_a) is found as $0.067h^{-1}$ under unsaturated soil condition. It was reported as $0.139h^{-1}$ in unsaturated soil condition by Hemalatha et al.,(2013) and $0.0022h^{-1}$ was reported by vanitha et al.,(2017) for the flooded condition. Bolado et al., (2005) reported the value of hydrolysis as $0.05h^{-1}$under unsaturated soil conditions. Urea hydrolysis rate constant is higher in unsaturated soil condition when compared with the flooded condition.

Distribution coefficient (K_d) is found as $0.668cm^3/g$ in unsaturated soil condition. It was reported as $0.0339cm^3/g$ under unsaturated soil condition by Hemalatha et al.,(2013) highest value of 0.9 cm^3/g was reported by vanitha et al.,(2017) for the flooded condition. Distribution coefficient for ammonium ranges 1 to $10cm^3$ /g as reported by Wagenet et al., (1977). Hongprayoon et al., (1991) reported a distribution coefficient of $0.03cm^3/g$ for a medium texture soil. Distribution coefficient is higher in flooded condition while compared with unsaturated soil condition.

The estimated ammonia volatilization (μ_v) coefficient is $0.013h^{-1}$. It was reported as $0.0083h^{-1}$ by Hemalatha et al.,(2013) and $0.0081h^{-1}$ by vanitha et al.,(2017). Al Kanani et al., (1991) reported first order coefficient for volatilization as 0.013 h^{-1} which were of the same order of magnitude as in our study. Ammonia volatilization is higher in unsaturated soil condition if compared with flooded soil condition. The higher temperature in unsaturated condition caused an increase in volatilization loss.

Nitrification rate (μ_n) constant is estimated at $0.0029h^{-1}$. It was observed as $0.0074h^{-1}$ by Hemalatha et al.,(2013) and the highest value of $0.01h^{-1}$ was observed by vanitha et al.,(2017) under flooded condition. Bolado et al., (2005) reported the value of nitrification as $0.002h^{-1}$ under unsaturated soil conditions. Anaerobic condition favored the nitrification process and caused a higher value of nitrification coefficient under flooded conditions.

CONCLUSIONS

Estimation of reaction rate constants is essential for nitrogen balance studies. With a minimum number of observations in the field four reaction rate constants for urea hydrolysis, distribution coefficient, ammonia volatilization, and nitrification were found out by using risk solver platform in MS-Excel environment. The estimated reaction rate constant of urea hydrolysis, distribution coefficient, volatilization, nitrification are $0.067h^{-1}$, $0.668cm^3/g$, $0.013h^{-1}$, and $0.0029h^{-1}$ respectively from the present study. Estimated values are matching the ranges reported in the literature. Urea hydrolysis and Ammonia volatilization are higher in the unsaturated soil condition than the flooded condition. Distribution coefficient and nitrification coefficient are higher in the flooded soil condition than the unsaturated soil condition.

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